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(54) Drilling fluids and methods of using them

(57) A naphthenic oil is used as the oil component of an oil based drilling fluid that is used for carrying out of a subsea bore hole debris that may then be dumped in the sea while still contaminated with the oil.

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SPECIFICATION

Drilling fluids and methods of using them

Drilling fluids are used to carry debris, such as drill cuttings, out of a bore hole during the drilling of the hole or during other operations within the hole. Thus the fluids are circulated down the hole and carry the debris up the hole. Throughout this specification we use the term "drilling fluids" in the generic sense to mean the fluids (sometimes called muds) that are intended to be used during the actual drilling of an oil well or other bore hole as well as the fluids that are intended to be used at other stages, for instance the work over or completion of a well, such other fluids sometimes being known as work over fluids or packer fluids.

The debris that is carried from the bore hole by the drilling fluids is separated from the fluid at the head of the hole and the fluid is recycled. The debris may be dumped.

The drilling fluids consist of a liquid phase and often contain also a solid phase dispersed in it, for instance a weighting agent such as barytes. The liquid phase may consist of water in which various minor additions may be dissolved or dispersed, e.g. various gelling agents and dispersing agents. However it is often found that best results are obtained, especially during drilling, when the liquid phase includes oil, the fluids then being referred to as oil based drilling muds or fluids. Thus the liquid phase may consist of oil or it may be a mixture of oil and water, for instance an oil-in-water emulsion or a water-in-oil emulsion.

Numerous oils have been proposed for use as the oil in the liquid phase of drilling muds. There have been some proposals to use vegetable or other edible oils but mineral oils have generally been considered as more satisfactory and cost effective. Various mineral oils have been proposed. A typical disclosure is in British Patent Specification No. 1,467,841 in which it is stated that the oil may be diesel oil, crude oil, kerosene or other aliphatic hydrocarbons or mixtures. Another appears in US Patent Specification No. 2,969,321 in which the proposed oils are topped crude oils, gas oils, kerosene, diesel fuels, heavy alkylates and fractions of heavy alkylates. Despite all these numerous proposals the oil was generally chosen having regard primarily to availability and cost effectiveness and as a result the oil that is used in practice is generally diesel oil.

Despite the actual use of diesel oil in practice there are some examples in the literature of particular oils other than diesel oils. For instance various asphaltic, paraffinic and naphthenic oils are exemplified in US Patent Specification No. 2,698,833 and in US Patent Specification No. 3,840,460 there is an example of an oil base that is a blend of sulphurised lard oil, chlorinated paraffin and a naphthenic mineral oil. The oils exemplified in US Patent 2,698,833 generally appear unsatisfactory by todays safety standards because of their generally low flash points and the oil exemplified in US Patent 3,840,460 suffers from the cost and other disadvantages incurred in the use of oils other than mineral oils.

When the drill cuttings or other debris are separated from the drilling fluid, e.g. at the well head, the resultant separated debris will still be contaminated with the fluid phase of the drilling mud, and therefore with the oil if it is an oil based drilling mud. When the drilling is at sea the further treatment of the contaminated debris can create a problem. If the contaminating oil is toxic to marine life and the contaminated debris is simply dumped into the sea then this dumping contaminates the sea unacceptably. Diesel oil has been shown to be toxic to marine life and so debris contaminated with diesel oil has to be washed before dumping but this requires extra apparatus on the rig or drilling platform and results in the generation of washings contaminated with oil, which in turn then have to be separated or treated further before they can be discharged.

In U.S. Patent No. 3,594,317 the problems arising from the anti-pollution regulations concerning the use of oils in drilling muds are discussed and it is stated that it has become necessary to find materials other than oil which will provide the attributes of oil in drilling mud. The proposal in that specification is to use decyl alcohol as a component of an aqueous based mud. Whilst this may avoid pollution problems decanol is not a satisfactory and cost effective alternative to oil in drilling muds, especially in the more difficult bore holes where sticking of, for instance, the drill pipe is a particular risk.

Recent tests in USA have indicated that the mineral seal oil available in USA from US refineries under the trade name Mentor 28 can be used in place of diesel oil as the oil in an oil based drilling fluid and that the resultant fluid is less toxic to marine life than fluids based on diesel oil. However Mentor 28 can be expensive and the toxicity of the fluids tested in USA still appears to be too high to be freely acceptable for dumping in the North Sea. Also it appears that the toxicity of the fluid may vary according to the source from which the Mentor 28 is obtained, and this renders it impracticable as a base for non-toxic drilling fluids. Another problem is that Mentor 28 is rather more viscous than diesel oil.

According to the invention we have now surprisingly found that naphthenic oils are, as a class, especially suitable for use as the oil of oil based drilling fluids intended for carrying debris out of a subsea bore hole, prior to dumping of the debris in the sea while still contaminated with the oil.

Naphthenic oils may be derived from naphthenic crude and it seems that they can be much less toxic to marine life than diesel oil and US Mentor 28. The naphthenic oil may be obtained by blending

two or more oils of which at least one generally is derived from naphthenic crude. For instance a blend may be formed of an oil derived from naphthenic crude and a paraffin oil, provided that the final blended oil can still be classified as a naphthenic oil. Naturally when blends are formed the blending oil must not be such as to introduce toxic components, and this is discussed in more detail below.

Suitable naphthenic crude for use as the source of some or all of the naphthenic oil is Venezuelan crude. The oil may have been hydrogenated during its production from naphthenic or other crude to convert aromatic compounds to naphthenes.

Naphthenic oils are a well recognised class of oils clearly distinguished from paraffinic oils. They are characterised by the fact that they contain less than about 70% paraffinic (aliphatic) compounds and a substantial amount of naphthenic (cycloaliphatic) compounds. For instance at least 25% and preferably at least 35 or 40% of the oil is provided by naphthenic compounds. Best results appear to be provided when the oil contains 30 to 60%, preferably 45 to 60%, naphthenic compounds, but higher amounts (for instance up to 70% or 80%) or lower amounts (for instance 25 to 30 up to 45%) are sometimes suitable. The paraffinic content is preferably not more than 65%, or 70% at the most.

The naphthenic oil preferably has a characterisation factor of less than 12.0 and preferably from 11.8 to 11.0 or even down to 10.0.

Preferably, the oil has an aromatic content of less than 5%, preferably less than 4% and most preferably 0.2 to 3.5%. The aromatic content of an oil may be recorded by various test methods. Typically it may be determined as the percentage by volume of the oil that is provided by aromatic compounds. It can be measured by calculating the proportion of carbon atoms in the oil that are present in aromatic compounds, based on the total proportion of carbon atoms in the hydrocarbon content of the oil. The contents of naphthenic and paraffinic compounds may be determined in the same manner. Suitable methods are ASTM D2140-66 and ASTM D2007.

Naphthenic oil derived from suitable naphthenic crude can have a satisfactorily low aromatic content but if the oil is obtained by blending then the oils blended into the naphthenic oil must not be such as to introduce toxic components. In general they should not be such as to increase the aromatic content above the values quoted since it seems that high aromatic contents are often associated with toxicity. Mentor 28 in USA seems to have an aromatic content of above 10%. However we believe that some low molecular weight aromatic compounds are non-toxic and that the toxicity probably arises from the presence of some or all of the polynuclear aromatic compounds, where poly represents at least 4 benzene rings and generally 5 or more, (especially benzopyrene and 1,2,5,6-dibenzanthracene) and some lower molecular weight compounds such as toluene, xylenes, phenanthrenes and possibly also naphthalenes. If these are absent then the total aromatic content can be higher than the 5% mentioned above and may be as high as 10 or even 12%. It is however safest, from the toxicity point of view, to have the aromatic content as low as possible, preferably below 2.5%.

The naphthenic oil is preferably substantially colourless and substantially odourless. It must of course comply with safety regulations and in practice this means that it must have a flash point of at least 60°C, preferably 66°C or more.

We have established that it is desirable, especially for subsea drilling, that the oil of the oil base should at 5°C, and generally also at 20°C, have a viscosity less than the viscosity of diesel oil. This is particularly important because of the low ambient temperatures encountered in many offshore drilling operations and the difficulties that follow from funnel and plastic mud viscosities that may be too high at ambient temperatures unless oils of very low viscosity are used. Generally the viscosity at 5°C is below 15, preferably below 10, for instance 1 to 7 cSt.

The viscosity at 20°C should be low, generally below 15 and preferably below 10, most preferably below 8. It is normally at least 1, typically from 3 to 8 and often 4 to 7 cSt. The oil of the oil base generally has a viscosity at 40°C of below 6 cSt and preferably below 5.5 cSt. This viscosity is often in the range 1 to 5.5, for instance 3 to 5. However there are indications that best results are obtained with very low values, preferably 1.2 to 3.8 cSt.

The oil preferably has a viscosity at 100°C of from 0.6—2.5, generally 0.7 to 1.4 cSt. All viscosity measurements herein are kinematic viscosity values obtained by ASTM 445.1P71.

The initial boiling point of the distillation range of the oil used as the oil base is preferably below 250°C. The A.P.I. gravity value of the oil is generally at least 15 and is normally below 35.

Four naphthenic oils suitable for use in the invention are 60 Solvent Pale and KL55 (also sold as Prospect 5) from J. O. Buchanan of Renfrew, Scotland, POLY-X-HP35 supplied by Burmah-Castrol Company and Clairsol 350 supplied by Carless Solvents of Hackney Wick, London. Typically analyses of these oils are as follows.

	60 Solvent Pale	KL55
Gravity A.P.I. at 15°C	30.2	32.2
Density g/cm³ at 15°C	0.875	0.864
Flash Point — closed cup	145°C	142°C
Pour Point	−57°C	−54°C
Colour (Sabolt)	24	15
Viscosity cSt at 40°C	7.7	6.6
Viscosity cSt at 100°C	2—2.1	1.9—2.0
Distillation — Initial Boiling Point	275°C	294°C
Final Boiling Point	350°C	329°C (95%)
Aniline Point	76°C	80°C
Sulphur Content	0.1—0.2%	less than 0.1
Paraffinic Content	48.2%	53.9%
Naphthenic Content	48.5%	42.2%
Aromatic Content (ASTM D2140)	3.2%	3.9%
Characterisation Factor	11.6	11.5

	POLY-X-HP35
Colour, Saybolt	+20
Density at 20°C	0.860
Kinematic Viscosity at 20°C cSt	6
Kinematic Viscosity at 40°C cSt	3.6
Viscosity at 100°C cSt	1.1
Flash Point (PMCC) °C	115
Pour Point °C	−66
Sulphur Content %	2.2
Aniline Point	91±1°C
Aromatic Content Atoms	6%
Naphthenic Carbon Atoms	54%
Paraffinic Carbon Atoms	40%

	Clairsol 350 Typical properties	Test method
Odour	Good	—
Colour	Water White	—
Viscosity at 20°C	2.3 cSt	ASTM D1298
Density at 15°C	0.788	ASTM D 86
Distillation Range °C		
Initial Boiling Point	200	
50% Distils at	221	
Dry Point	248	ASTM D93
Flash Point °C	74	ASTM D1133
Kauri Butanol Value	28	CSL 606-4
Aromatic Content v/v	0.2%	—
Low Explosive Limit (% volume in air)	0.6	—
Upper Explosive Limit (% volume in air)	7.1	—
Autoignition Temperature °C	230	
Naphthenic content	40% v/v	
Isoparaffin content	20% v/v	
n-paraffinic content	40% v/v	
Threshold Limit Value (TLV) ppm	200	by calculation

Other oils having similar analysis may be used especially other naphthenic solvents, for instance having characteristics similar to Clairsol 350.

Any of these oils can be used individually or blends can be formed of two or more of these oils or of one or more of these oils with another oil, for instance a paraffinic oil. A suitable blend is formed of 40 to 90, preferably 60 to 80, parts by volume of a naphthenic oil with a paraffinic oil, provided the blend still has a sufficiently high naphthenic content to be classed as a naphthenic oil.

A suitable oil for use in the invention is formulated by blending 70 parts by volume of 60 Solvent Pale oil and 30 parts by volume of Clairsol 350. The resultant blended naphthenic oil has the following properties.

	Typical properties
Aniline Point	75.4°C
Flash Point	96°C
Pour Point below	−50°C
Viscosity at 40°C	4.19 cSt
Distillation range — initial boiling point	214°C
10% boiling	236°C
50% boiling	292°C
90% boiling	320°C
Final boiling point	335°C
Estimated aromatic content	2.37%
Specific gravity	0.849

A characteristic of the defined oils is that, compared to the toxicity of diesel oil, they are substantially non-toxic if they are dumped in the sea in relatively small quantities, e.g. as contamination on cuttings that have been separated from drilling fluid. Toxicity can be observed by determinining the effect of a selected amount of the oil in sea water on brown shrimps (*Crangon crangon*). Healthy shrimps are maintained in aerated sea water at 15°C in the presence of a selected concentration of the oil and the mortality of the shrimps after varying periods is observed. On this test diesel oil gives high mortality, e.g. above 50% and often 90 to 100% at a concentration of 100 μl/l after 24 hours. The oils used in the invention preferably give substantially no mortality (for instance below 10% and preferably below 1%) at 24 hours when present in amounts of 100 μl/l and preferably also substantially no mortality when used in amounts of 333 μl/l for 24 hours. Preferably the mortality at 96 hours at 100 μl/l is also low, generally being below 30% and preferably below 15% and preferably also the mortality at 333 μl/l at 96 hours is in the same range, most preferably below 15%. Generally the toxicity is such that at least 50% of the brown shrimps survive for at least 5 days at oil concentrations of at least 333 μl/l and often of at least 1000 μl/l. A typical diesel oil, No. 2 diesel oil, results in only 50% survival after as little as 5.6 hours at a concentration of 100 μl/l.

The oil base of the drilling fluid may consist of the described mineral oil or it may be a blend of the described mineral oil and water. At least 1% by volume of this blend must be the mineral oil and generally the amount of oil is at least 30% by volume based on water plus oil, with the amount preferably being from 51 to 99%, most preferably 60 to 95% by volume oil, with the balance to 100% by volume being water. Depending upon the emulsifiers present and the amounts of oil and water the fluid may be a water-in-oil emulsion or an oil-in-water emulsion.

The water used for forming the fluid may be fresh water or sea water and may contain dissolved salts such as sodium chloride or calcium chloride, up to saturation concentrations. Thus the fluid may be an oil-in-water emulsion in which the water is a sodium chloride brine. An advantage of the use of the defined oils is that emulsions formed from them tend to be more stable than the corresponding emulsions formed from other, relatively non-toxic, mineral oils such as various paraffinic oils.

The drilling fluids may contain other additives as is conventional in oil based drilling fluids and these additives may be dissolved or dispersed in the oil base. Thus they may contain one or more emulsifiers, for instance, polymerised organic acids such as the product sold by the Applicant under the Trade Name Carbotec L and oil soluble amide polymers that are wetting agents and supplementary emulsifiers, such as the product sold by the applicant under the Trade Name Carbo-Mul. The amount of any emulsifiers is generally from 0.1 to 10% (of the commercial emulsifier) by volume, most preferably 1 to 5% by volume, based on the total volume of oil and water, or 1 to 20%, preferably 2 to 5% based on the water.

The mud may contain high molecular weight organic polymers and inorganic bridging agents, such as the mixtures sold by the Applicants under the Trade Name Carbo-Trol. Lime hydrate may be dissolved in the water.

The drilling fluids will, in particular, generally contain a large amount of weighting material, such as barite, iron oxide, siderite or calcite. The amount of weighting aid is generally from 100 to 400 grams per 100 cc drilling fluids, for instance 200 to 500 pounds per barrel.

It is standard practice to adjust the rheological properties of oil based and other drilling fluids by including gelling agents in them. A variety of materials have been proposed as gelling agents. The most widely used gelling agents are bentonites, for instance the material commercially available as DMB (drilling mud bentonite) and the products available as Sedapol 155 or Sedapol 44, or Claytone 34 or Claytone 40. They can be used in the invention but better results are obtained by use of an organophilic hectorite.

This may be a naturally occurring hectorite or synthetic hectorite, for instance as described in British Patent Specification No. 1054111. If it is a synthetic hectorite it preferably includes exchangeable organic ammonium cations as described in British Patent Specification No. 1121501.

The preferred materials may be described as tetraalkylammonium hectorites, as described in British Patent Specification No. 1121501. One to three of the alkyl groups are preferably short chain

alkyl groups (e.g. C_{1-6} most preferably C_{1-3}, typically methyl) and one to three of the alkyl groups are preferably long chain alkyl groups (e.g. C_{10-25}, typically C_{14-22}, most preferably C_{18}).

A preferred material is dimethyldioctadecyl ammonium hectorite, preferably Bentone 38 or Imvitone 1 or Imvitone 2, which are derivatives of naturally occurring hectorite.

The amount of gelling aid is typically from 1 to 10, most preferably 1.25 to 4, grams gelling aid per 100 cc fluid. An alternative way of expressing the amount is as 3 to 15, most preferably 5 to 9, pounds gelling aid per barrel drilling fluid. In general the amount of gelling aid required in the fluids of the invention is greater than the amount required in conventional drilling fluids, for instance being from 1.5 to 2.5 times the amount required when the oil is diesel oil.

The following are examples of the invention.

Example 1

A drilling fluid is prepared containing 212 cc Pale Oil 60 as defined above, 7 cc blown tall oil emulsifier, 5 cc oil soluble amide polymer as secondary emulsifier, 53 cc water containing 25% calcium chloride, 6 g lime hydrate, 7 g of a blend of high molecular weight organic polymers and inorganic bridging agents, 358 g barite and 6 g dimethyldioctadecyl ammonium hectorite.

Its properties are measured before and after hot rolling at 122°C for 17 hours (H/R). The results are set out in the following table. ES is electrical stability.

Mud No.	1	H/R	H/R
Mud Weight	14.5	14.5	14.5
Flow Prop. Test temp °C	49	49	65
Fann Readings rpm 600	223	226	125
300	128	130	71
200	95	94	52
100	59	55	32
6	16	13	9
3	14	10	8
Plastic Viscosity cp	95	96	54
Yield point g/100 cm²	16	17	8
Gel strength g/100 cm²	8/12.5	6/11.5	4/7.5
E.S. volts at 49°C	1430	1160	

When the oil was tested for toxicity by the method described above, it was found that after 96 hours it caused about 3% fatality at 333 μl/l and up to 15% fatality after 120 hours. In the same tests number 2 Diesel oil gives 93% fatality after 24 hours and 100% fatality after 72 hours at 100 μl/l, and the paraffinic oil sold as Mentor 28 gives about 59% fatality after 96 hours at 333 μl/l.

Example 2

A drilling fluid is prepared having the same composition as above except that the amount of Pale Oil 60 is 149 cc and this is blended with 63 cc Clairsol 350. Very satisfactory downhole and toxicity properties are obtained when used in a subsea bore hole followed by filtration of the debris from the fluid and dumping of the debris in sea.

Example 3

A drilling fluid is prepared as in Example 1 except that POLY-X-HP35 is used in place of the Pale Oil 60. The resultant fluid had particularly good properties under high downhole temperature conditions.

Example 4

A drilling fluid was prepared by blending 235 cc Clairsol 350, 5 cc primary emulsifier, 5 cc secondary emulsifier, 9 grams gelling aid, 42 cc calcium chloride brine, 5 grams lime, 15 grams bridging aid and 309 grams barytes. This drilling fluid is a 13 pound per gallon mud having an 85:15 oil:water ratio and an internal phase activity of 0.75. Its initial properties at 49°C were plastic viscosity 22 cps, yield point 5.5 g/100 cm² and gel strength 3/6.5 g/100 cm² and after hot rolling at 65°C were plastic viscosity 23 cps, yield point 7 g/100 cm² and gel strength 5/6.5 g/100 cm². It is particularly suitable for use in subsea drilling where the sea temperature may be 5°C or lower.

Example 5

A drilling fluid is prepared as in Example 2 using a bentonite gelling aid in place of the hectorite. The resultant fluid is less satisfactory when it is allowed to cool to, say, 5°C but still gives useful downhole properties.

It should be noted that best results are obtained when the oil has an aromatic content of below 15, and preferably below 5 and most preferably below 1% by volume when measured by ASTM 2007 (especially when the oil is a naphthenic solvent) or, if it is an insulating oil, when its aromatic content is

below 5% when measured by ASTM 2041. When measured by infra red the aromatic content may be below 10, preferably below 6, for instance 0.1 to 5% (compared to about 12% for US Mentor 28 and 18—20% for Diesel).

Claims

1. A method in which an oil based drilling fluid is used to carry debris out of a subsea bore hole and the debris is then dumped in the sea while contaminated with the fluid, in which method the oil of the oil base is a naphthenic oil.

2. A method according to claim 1 in which the oil has a naphthene content of 30 to 70%.

3. A method according to claim 1 or claim 2 in which the oil is derived from a naphthenic crude.

4. A method according to claim 1 or claim 2 in which the oil is a blend of an oil derived from a naphthenic crude with a paraffinic oil.

5. A method according to any preceding claim in which the oil contains not more than 5% aromatic compounds.

6. A method according to any preceding claim in which the oil contains not more than 2.5% aromatic compounds.

7. A method according to any preceding claim in which the oil has a viscosity at 40°C of less than 6 cSt.

8. A method according to any preceding claim in which the oil has a viscosity at 20°C less than 10 cSt.

9. A method according to any preceding claim in which the oil has a viscosity at 40°C of from 1 to 5.5 cSt and at 20°C of from 1 to 7 cSt and at 100°C of from 0.7 to 2.5 cSt.

10. A method according to any preceding claim in which the oil is less viscous at 20°C than diesel oil.

11. A method according to any preceding claim in which the oil is selected from 60 Solvent Pale, KL55, POLY-X-HP35 and Clairsol 350 and oils having substantially the same properties as any of these, and blends of two or more such oils.

12. A method according to any preceding claim in which the oil gives a mortality of brown shrimps of below 5% when tested in aerated sea water at 15°C for 24 hours at a concentration of 333 μl/l.

13. A method according to any preceding claim in which the oil is substantially free of benzopyrene and 1,2,5,6-dibenzanthracene and other polynuclear toxic aromatic compounds.

14. A method according to any preceding claim in which the oil base consists of 30 to 100% by volume of the naphthenic oil and 70 to 0% water and the drilling fluid also includes drilling fluid additives selected from gelling agents, emulsifiers, bridging agents, weighting agents and lime.

15. A method according to any preceding claim substantially as herein described with reference to any of the examples.

16. An oil for use as the oil in an oil based drilling fluid and which is a naphthenic oil.

17. An oil for use as the oil in an oil based drilling fluid for carrying out of a subsea bore hole debris that is then dumped in the sea, and in which the oil is a naphthenic oil.

18. An oil according to claim 16 or claim 17 and which is as defined in any of claims 2 to 13.

19. An oil according to claim 16 or claim 17 substantially as herein described with reference to any of the examples.

20. An oil based drilling fluid in which the oil of the oil base is a naphthenic oil.

21. An oil based drilling fluid for carrying out of a subsea bore hole debris that is then dumped in the sea and in which the oil of the oil base is a naphthenic oil.

22. A drilling fluid according to claim 20 or claim 21 and which is as defined in any of claims 2 to 14.

23. A drilling fluid according to claim 20 or claim 21 substantially as herein described with reference to any of the examples.

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